PATENT SPECIFICATION

650,947

Date of filing Complete Specification: Sept. 20, 1948.

Application Date: Sept. 19, 1947. No. 25562/47.

Complete Specification Published: March 7, 1951.

Index at acceptance:—Classes 2(iii), B2; and 2(v), R18p.

PROVISIONAL SPECIFICATION

The Production of New Polymers

I, MICHAEL MOJZESZ SZWARC, a Palestinian Citizen, of 33, King's Road, Prestwich, Manchester, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production of new polymers.

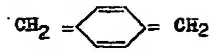
In accordance with the invention new polymers are produced by the pyrolysis of the vapour of a mono- or polycyclic aromatic compound having two substituted methyl groups in the 1:4 or para positions and the subsequent cooling of the resulting vapours. Example of compounds which may be used in this process are para-xylene and 1:4 dimethyl naphthalene. The invention also includes the new polymers produced by this process.

Thus in accordance with the invention a new polymer is produced by the pyrolysis of para-xylene vapour and the cooling of the pyrolysed vapours.

The pyrolysis should be carried out under such conditions that the pressure exerted by the vapour of the aromatic compound is below atmospheric pressure, and preferably below 200 mm. mercury. This may be achieved by diluting the vapour of the aromatic compound with an inert carrier gas such as nitrogen so as to maintain a low partial pressure of the aromatic compound or by working under reduced pressure.

The pyrolysis of para-xylene vapour in accordance with the invention is carried out at a temperature of from 700° C. to 1000° C. and preferably of from 750° C. to 900° C. and the vapour is subjected to this temperature for from 0.05 to 10 seconds and preferably for from 0.3 to 1 second.

Experiments carried our by reacting the pyrolysed vapours of para-xylene with iodine vapour have shown that para-xylylene-di-iodide ($CH_2I.C_6H_4.CH_2I$) is formed. This would indicate that the radical $CH_2.C_6H_4.CH_2$ exists in the vapour phase in the pyrolysed vapours, probably in the form



and is the monomer of the product obtained from para-xylene by the process of the invention.

The temperature to which the monomer vapour formed by the pyrolysis should be cooled for polymerisation to take place depends on the vapour pressure of the monomer in the gaseous phase. This temperature should be such that the corresponding saturation pressure of the monomer vapour is less than the partial vapour pressure of the monomer in the gas stream. Polymerisation takes place spontaneously on condensation of the polymer. The condensation and consequent polymerisation may take place in successive stages at progressively reduced temperatures.

In one example of the process of the invention, para-xylene vapour at a pressure of 4 to 10 mm. mercury was passed through a tube heated to 860° C. at such a rate that the vapour was subjected to this temperature for from 0.3 to 0.8 seconds. The vapours leaving the tube were passed into a trap in which they were cooled to 0° C. in contact with a cold surface on which the polymerised product was deposited in the form of a white, occasionally transparent film.

The yield of polymer was 12% by weight of the para-xylene treated. Unconverted para-xylene was also condensed in the trap.

The polymer produced from para-xylene in accordance with the invention is insoluble in boiling benzene or toluene, resistant to sulphuric acid at 100° C. and has great thermal stability. It does not soften when heated up to 175° C.

Dated this 19th day of September, 1947.

N. GAVRON,
Agent for the Applicant.

COMPLETE SPECIFICATION

The Production of New Polymers

I, MICHAEL MOJZESZ SZWARC, a Palestinian Citizen, of 33, King's Road, Prestwich, Manchester, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of new and useful polymers.

The invention consists in a process for the production of a solid polymer in which the vapour of an aromatic hydrocarbon having a single benzene nucleus or two condensed benzene nuclei in the molecule and having two methyl groups substituted in the para positions of one benzene nucleus, is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

The invention also consists in a process for the production of a solid polymer in which the vapour of para-xylene is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

The invention also consists of a process for the production of a solid polymer in which the vapour of 1.4 dimethyl naphthalene is pyrolysed by being subjected to a temperature between 700 and 1000°C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

The pyrolysis step of the process of the invention is preferably carried out by subjecting the vapour of the aromatic hydrocarbon to a temperature between 700 and 1000° C. for from 0.1 to 1 seconds. The temperature of pyrolysis is preferably between 700 and 900° C.

High pressures e.g. pressures above about 3 atmospheres should be avoided in carying out the process of the invention. Preferably the pressure exerted by the vaopur which is subjected to pyrolysis is in the region of atmospheric pressure or below. The vapour subjected to pyrolysis may be diluted with an inert carrier gas such as nitrogen or carbon dioxide in order to maintain a low partial vapour pressure of the aromatic hydrocarbon.

Experiments carried out by reacting the pyrolysed vapours of para-xylene with iodine vapour have resulted in the production of para-xylylene di-iodide

$(CH_2I.C_6H_4.CH_2I)$.

This indicates that the radical

$CH_2.C_6H_4.CH_2$

exists in the vapour phase in the pyrolysed vapours and it appears that this radical is the monomer of the polymer obtained by applying the process of the invention to para-xylene. The ratio of carbon to hydrogen in the polymer as determined by analysis confirms this view.

Similar experiments carried out with the pyrolysed vapours of 1.4 dimethyl naphthalene show that the monomer (existing in the vapour phase) of the polymer obtained in this case consists of naphthalene with two CH_2 groups substituted in the 1.4 positions.

Polymerisation takes place spontaneously on condensation of the monomer vapour by cooling. The cooling may take place in contact with a cool surface on which the polymer is deposited in the form of a film.

Broadly stated, the recurring units or monomers of the polymers produced by the process of the invention are compounds (which apparently exist in the vapour phase only) having one benzene nucleus or two condensed benzene nuclei in the molecule and having two CH_2 groups substituted in the para positions of one benzene nucleus. It is possible that some cross-linking may occur in the polymers although the X-ray patterns of the polymers produced show no definite evidence of such cross-linking.

The invention also consists in the polymers produced by the processes referred to above.

The temperature to which the monomer vapour formed by pyrolysis should be cooled for condensation and polymerisation to take place can easily be determined by experiment. It depends on the partial vapour pressure of the monomer in the gas phase. The upper limit increases with increasing partial vapour pressure. Generally speaking, the operative temperature range for cooling will be between room temperature and −80° C. though higher temperatures may be found effective with high partial pressures of the monomer.

Condensation and polymerisation may take place in successive stages at progressively reduced temperatures, that is the vapours leaving the first condensation and polymerisation stage are further cooled to condense and polymerise a further portion of the residual monomer vapour and so on.

Following are examples of processes for

the production of new polymers in accordance with the invention:

EXAMPLE 1.

Para-xylene vapour at a pressure of 8 to 10 mm. Hg. was passed through a tube heated to 860° C. at such a rate that the vapour was subjected to this temperature for from 0.3 to 0.4 seconds. The vapours leaving the tube were passed into a trap in which they were cooled to 0° C. in contact with a cold surface on which the polymerised product was deposited in the form of a white occasionally transparent film.

The yield of polymer was approximately 12% by weight of the para-xylene treated. Unconverted para-xylene was also condensed in the trap.

EXAMPLE 2.

Para-xylene vapour at a pressure of 150 mm. Hg. was passed through a tube heated to 820° C. at such a rate that the vapour was subjected to this temperature for about 0.1 seconds. The vapours leaving the tube were cooled to room temperature and the polymerised product was deposited.

The polymer was in the form of a film similar to that obtained in Example 1.

EXAMPLE 3.

Carbon-dioxide at atmospheric pressure was bubbled through liquid para-xylene maintained at 100° C. to take up para-xylene vapour so that the partial pressure of the latter in the mixture was about 100 mm. Hg. The mixture of carbon-dioxide and vapour was then passed through a tube heated to 800° C. at such a rate that it was subjected to this temperature for 1 second. The gaseous mixture leaving the tube was cooled to room temperature in a trap in which the polymer was deposited in the form of a white occasionally transparent film.

EXAMPLE 4.

1.4 dimethyl naphthalene vapour at a pressure of about 10 mm. Hg. was passed through a tube heated to 860° C. at such a rate that the vapour was subjected to this temperature for from 0.3 to 0.4 seconds. The vapours leaving the tube were passed through a trap in which they were cooled to room temperature. The polymerised product was deposited in the trap in the form of a white film.

All the polymers obtained in the above examples had great thermal stability and did not soften when heated up to a temperature of 270° C. They were insoluble in, and also did not swell visibly in, boiling ethyl alcohol, diethylether, chloroform, xylenes, benzene, toluene, glacial acetic acid.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for the production of a solid polymer in which the vapour of an aromatic hydrocarbon having a single benzene nucleus or two condensed benzene nuclei in the molecule and having two methyl groups substituted in the para positions of one benzene nucleus, is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

2. A process for the production of a solid polymer in which the vapour of para-xylene is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

3. A process for the production of a solid polymer in which the vapour of 1.4 dimethyl naphthalene is pyrolysed by being subjected to a temperature between 700 and 1000° C. for not more than 10 seconds and the resulting vapours are cooled to a temperature at which a solid polymer is deposited.

4. A process as claimed in any of the preceding Claims in which the pyrolysis is carried out with the vapour of aromatic hydrocarbon exerting a pressure in the region of atmospheric pressure or below.

5. A process as claimed in any of the preceding Claims in which the pyrolysis is carried out at a temperature between 700 and 900° C.

6. A process as claimed in any of the preceding Claims in which the vapour of the aromatic hydrocarbon is subjected to the temperature of pyrolysis for from 0.1 to 1 seconds.

7. A process as claimed in any of the preceding Claims in which after pyrolysis the resulting vapours are cooled in contact with a cold surface to a temperature at which the polymer is deposited on the said surface in the form of a film.

8. A process as claimed in any of the preceding Claims in which the pyrolysis is carried out with the vapour of the aromatic hydrocarbon diluted with an inert gas.

9. A process as claimed in any of the preceding Claims in which the resulting vapours are cooled to a temperature between room temperature and −80° C.

10. A process for the production of a polymer substantially as described in any one of examples 1 to 4.

11. A process for the production of a

polymer substantially as hereinbefore described.

12. The polymer produced by the process claimed in any of the preceding Claims.

Dated this 10th day of September, 1948.

N. GAVRON,
Agent for the Applicant.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1951.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 2s. per copy; by post 2s. 1d. may be obtained.

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